

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
25 January 2001 (25.01.2001)

PCT

(10) International Publication Number
WO 01/05913 A1

(51) International Patent Classification⁷: C10L 9/10, (81) Designated States (*national*): AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW.

(21) International Application Number: PCT/DK99/00409

(22) International Filing Date: 16 July 1999 (16.07.1999)

(25) Filing Language: English

(26) Publication Language: English

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(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

— *With international search report.*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

A1

(54) Title: PHOSPHOR ADDITION IN GASIFICATION

WO 01/05913

(57) Abstract: The present invention provides a method useful in combustion, gasification or pyrolysis processes. The method is useful for the thermal treatment of carbonaceous fuels containing the inorganic species potassium and/or sodium. The method may be utilized for combustion, gasification or pyrolysis processes for conversion of biomass, coals, waste materials or chars of the above mentioned materials prepared by pyrolyzing the original material. The residual materials may act as a fertilizing agent and thus the value of the residual materials is improved. The method utilizes phosphor, in the form of phosphoric acid or salts of phosphor. The alkali and alkali earth metals in the fuel reacts with the added externally provided phosphor, which may be added in the form of phosphoric acid, phosphor oxides or salts of phosphor. The alkali or earth alkali metals are in the here proposed process converted to phosphates, ortho-phosphates, potassium phosphate, sodium phosphate, calcium phosphate, potassium calcium phosphates or calcium hydrogen phosphate. The resulting compositions strongly reduce alkali induced corrosive effects, and have

Phosphor addition in gasification

TECHNICAL FIELD

This invention relates to the pyrolysis, combustion and gasification of carbonaceous materials such as biomass, i.e. straw, wood or peat, oil, petroleum residua, waste, coals, coke or char, or combinations of the above mentioned. The invention improves combustion, gasification or pyrolysis processes carried out in the presence of alkali metals and alkali metal compounds. More particularly the invention comprises adding phosphorous compounds to combustion, gasification or pyrolysis processes in order to react with the alkali compounds. The residual products from this reaction can be used as a cheap fertilizing agent. Furthermore, this process reduces the amount of corrosive alkali components in the reactor. ELKRAFT A.m.b.A. and the Danish Ministry of Environment and Energy have supported the research work through the Energy Research Programme (EFP).

BACKGROUND

It is well known that certain alkali metal compounds have a low melting temperature and therefore leads to problems with sintering when biomass, which have a high alkali content, is combusted, gasified or pyrolysed. Silicon is another element typically abundant in the fuel or as a bed material added to fluidized-bed systems as silica. Alkali compounds in combination with silica and possibly small amounts of calcium can produce low-temperature eutectica. These may cause severe agglomeration and sintering in combustion, gasification and pyrolysis reactors; in particular at temperatures above 750°C. Besides alkali compounds, which condense on cold spots in the reactor or downstream of the reactor, can cause corrosion problems.

$K_2O \cdot 4SiO_2$ melts at 765°C. $K_2O \cdot 4SiO_2$ mixed with small amounts of $CaO \cdot SiO_2$ produce an eutectica below 750°C. Also $K_2CaSi_3O_8$ have been measured in the sintered bed material. The melting of inorganic compounds into sintering particles causes bed defluidization and diminish the carbon-catalyst contact. Additional $CaCO_3$ have been shown in laboratory scale to cause significant neck growth between the particles (Skrifvars 1994, 1997) which can lead to agglomeration in the bed. Information about melting temperatures for several inorganic mixtures including oxides of Si, Ca, K and Na can be found in Levin [1985]. See the diagrams: fig. 391, 395, 401 and 485. One way of preventing agglomeration is to use additives in the process in order to convert the harmful alkali species. A number of possible additives are known. Such additives should be abundant and cost effective in use and during their use result in products with a useful and valuable property e.g. as a fertilizer. Anti-agglomeration agents in biomass typically deactivate the catalyst. The aim is, however, to maintain as much catalytic effect as possible and at the same time avoid severe agglomeration and sintering during the combustion, gasification or pyrolysis process.

REATECH's INVENTION

ReaTech's invention improves the combustion, gasification and pyrolysis process in an economical way and increases the value of the residual products.

Observation in our laboratory lead to the proposal that for fuels containing large amounts of potassium and sodium together with calcium and silicon, the melting temperatures are increased and the ash properties improved by the addition of phosphor compounds said in the form of phosphoric acid, H_3PO_4 , or calcium di-hydrogen phosphate, $Ca(H_2PO_4)_2 \cdot H_2O$ or $H_4P_2O_7$.

The phosphorous containing additive may be added alone or directly to the fuel as a liquid, slurry, solid, powder, granular material or as a gas. The phosphorous containing addi-

tives may be added in combination with the fuel and added catalyst and bed material in such amounts that the product phosphorous compounds are sufficient abundant to prevent agglomeration and sintering to take place. The amount of phosphorous addition depends on the process conditions, bed material, externally added catalyst and the inherent ash composition. The maximum needed amounts of moles total phosphorous added to the process necessary to prevent agglomeration and sintering will typically be equal to the sum of the molar contents of the alkali metals and the earth alkali metals introduced to the reaction zone. In simple cases the maximum amount is equivalent to the molar amounts of alkali and earth alkali metals inherent in the fuel. In most cases half or less of this amount is sufficient. In specific cases the amount, type and form of other additives or bed material must be considered. One typical bed material in a circulating or a bubbling fluid bed reactor is calcium carbonate, which will also partly react with phosphate to calcium phosphate. In case $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ is introduced as an additive, parts of the calcium herein will also react with the phosphate during the conversion process.

Using SEM-EDX ourselves, FTIR light scattering together with M.Sc. Jimmy Bak [1999] and X-ray diffraction together with Dr. Poul Norby [1999], we have found K_3PO_4 , in residual products in accordance with predictions from equilibrium calculations and also $\text{Ca}(\text{HPO}_4)_2$, $\text{KCa}(\text{PO}_4)_2$.

A number of these compounds provide a weak catalytic activity without contributing to severe agglomeration and sintering through the reaction with silica. Several tests have been made at the laboratory of ReaTech and at the Department of Energy Engineering (DTU, Denmark). The resulting phosphorous containing compounds prevented melt formation and thus the addition of phosphorous decreases the agglomeration and sintering problems otherwise observed without addition of phosphorous.

All naturally occurring phosphorous minerals are (ortho) phosphates and several phosphates are derived from phosphate rock. Phosphorous is thus a non-renewable resource. Large amounts of phosphate are however utilized as a fertilizer and the phosphate utilized in the present process will after withdrawal from the reactor and with or without additional treatment substitute phosphates added directly to soils as fertilizers. Information about several relevant phosphorous containing mixtures and their melting temperatures can be found in Levin [1985]. See the following diagrams: Figure 246-248, 536-540, 665-668, 959, 960-962. If abundant amounts of sodium is present, certain species may give low temperature eutectics, see Levin [1985]. These compounds have however not been detected for the relevant process conditions and Na seems in general to occur as gaseous NaCl .

PRESENT STATE OF ART

The addition of phosphorous to processes involving conversion of carbonaceous material has been used by a number of other groups. In US5538929 a preparation method for producing a phosphorous treated activated carbon (containing 2.5% to about 10% by weight of phosphorous support) is shown. An already activated carbon is used as a raw product. After preparation activated carbon is suitable as a carbon based catalyst support for use in a wide range of catalytic applications. In the present invention by ReaTech, phosphorous compounds (eventually together with various catalysts) are either directly added, or added together with a carbonaceous fuel, to the combustion/gasification/pyrolysis reactor, where the carbonaceous fuel is being gasified-/combusted/pyrolysed. The product of the process is (besides a gasification gas) an ash containing phosphorous in various forms together with other ash compounds. The ash also contains small residual amounts of carbon. The phosphorous compound reacts with alkali and earth alkali compounds in the fuel hereby preventing the alkali and the earth alkali compounds from reacting to compounds causing severe agglomeration, sintering and corrosion.

In patent US4458095 zinc and copper (I) salts comprising halides, carbonates, sulfates, acetates and phosphates are utilized for a pyrolytic conversion of rubber and waste, which

results in reduced level of sulfur and nitrogen impurities in the products. Zinc and copper (I) salts are not used in the present invention.

In JP52042806 a method comprising heating waste at 400°C in the presence of acidic catalyst (e.g. phosphoric acid treated silica) is described. The waste (e.g. polyethylene) is decomposed into paraffin wax containing oil and gaseous products. Paraffin is recovered from the oil (containing approximately 80 wt.% wax) and the gas is used as a fuel for the reactor. In gasification the anti sintering effect is interesting for process temperatures above 500°C.

In JP58167682 in the presence of at least one compound selected from phosphate, sulfate, nitrate or halide of Group VIII is added to a hydrogenation process (500-950°C) with a hydrogen pressure of 35-250 kg/cm². A carbonaceous substance (e.g. pulverized coal) is hydrogenated. Group VIII phosphate compounds accelerates the conversion of carbonaceous substance. It is not a part of the present invention to convert carbonaceous material in a hydrogenation process.

In JP54151585 a catalyst is carried by an inorganic heat resistant paint formulated metal oxide pigment. The carrier consists of alkali metal silicate (sodium silicate) and acidic metal phosphate, which has an excellent heat resistance. The catalyst is used to modify the gasification gas in order to minimize deposition of carbon and formation of tar. It is not a part of the present invention to add phosphate carried by an inorganic carrier consisting of alkali metal silicate and metal phosphate, and the purpose is different.

In JP2258067 a catalyst composed of a ceramic-supporting material wherein catalyst-components are described. This catalyst is immersed for promoting combustion of petroleum and prevents generation of free-carbon, hydrocarbon and CO gas. The catalyst may be the silicate of alkali metal or metal phosphate or metals of Pt family. Together with this composition a substance activating the catalyst is included. The present invention does not include the use of a ceramic supporting material to add phosphate carried by an inorganic carrier.

In JP56070875 a coating capable of preventing deposition of carbonaceous matter, are formed by coating a minute inorganic paint in which metal phosphate is used as a binder, on the surface of metal base, followed by drying, further coating a paint in. In this paint is dispersed a fatty acid-gasification decomposing catalyst with metal phosphate as binder, and sintering so as to form a coated layer. The catalyst is e.g. Na₂O, K₂O, CaO and MgO. The invention made by ReaTech does not add a paint that is used as a coating.

In JP53136007 it is described how to produce a specially mixed fuel containing oil base and water. The oil base and water is separately contacted with acid (e.g. nitric acid, sulfuric acid, acetic acid, phosphoric acid, hydrofluoric acid) or alkaline catalyst (e.g. alkali and alkali earth metals) and then mixed under agitation and pressure. The mixed fuel is used for boilers and internal combustion engines. The invention by ReaTech adds phosphorous components to a process without preliminary mixing these components into separate fuels that are following mixed and thus the present method deviates significantly from the method presented in JP53136007.

In EP00052334 a technique is presented, where carbonaceous materials are heated slowly to a conversion temperature of 200-600°C. The heating procedure is made at air exclusion conditions. The heating rates are specified to be from 5 to 30°C per minute. The products of the process are e.g. oil and carbon that may be used either for combustion or other purposes. As possible catalysts phosphoric acid and phosphate are mentioned but not alkali or earth alkali metals. The invention made by ReaTech adds phosphorous components to a gasification or combustion process. Air exclusion is not necessary, the heating rate may be rapid and the maximum reactor temperature is above 500°C, where agglomeration and sintering may become a problem if the reactor is operated without additive.

[Janson et al. 1996] describes a phosphate-based pulping of agrofibre including papermaking and spent liquor recovery. Trisodiumphosphate, Na₃PO₄, is used as a pulping and bleaching chemical in papermaking. A regenerative process is described. It is claimed that

after cleaning the phosphate spent liquors from silica, the spent liquor can, if necessary, be burned in fluidized bed or gasification plants. [Zevenhoven et al. 1999] states that in a pressurized gasification of biomass, phosphates are always present as $\text{Ca}_3(\text{PO}_4)_2$ with a high melting point of 1780°.

The invention by ReaTech does not involve the use of Na_3PO_4 as a bleaching chemical. It is not necessary to remove silicates from the process and phosphate is seen in several other forms than $\text{Ca}_3(\text{PO}_4)_2$, in particular phosphates occur in the forms of potassium or sodium compounds. The phosphorous agents, in the invention by ReaTech, are added to the process in order to react with potassium, sodium and calcium compounds and hereby avoid sintering and agglomeration in the bed.

MODE FOR CARRYING OUT OF THE INVENTION

The precise amount of added phosphorous said as phosphate depends on the precise process conditions, the fuel composition as well as the amount and composition of other additives and the specification of the quality of the residual product. Normally the amount of additive is minimized due to economic reasons. Sufficient amounts are however such amounts that introduces enough phosphorous to react with most alkali components in the process. Simple stoichiometric relations can also be utilized in combination with the valuable operational experience that is obtained from running full-scale reactors. The maximum needed amounts of moles total phosphorous added to the process necessary to prevent agglomeration and sintering will typically be equal to the sum of the molar contents of the alkali metals and the earth alkali metals introduced to the reaction zone. In simple cases the maximum amount is equivalent to the molar amounts of alkali and earth alkali metals inherent in the fuel. In most cases half or less of this amount is sufficient. In specific cases the amount, type and form of other additives or bed material must be considered. An estimate of the needed amount can be calculated using an equilibrium program like HSC, Roine [1997]. HSC calculates equilibrium compositions using a minimization method for Gibbs free energy and use a database based on thermochemical data like Barin [1995] and Knacke et al. [1991]. Other equilibrium programs are Chemsage and FACT. These programs can together with process knowledge be used to estimate the needed amount of additive to the process.

Phosphor addition in gasification

Reference cited

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JP2258067, Nishi Nihon Trust K.

JP56070875, Matsushita Elec. Ind. Co. LTD.

JP53136007, Hankona LTD.

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Zevenhoven-Onderwater M., Skrifvars B.-J., Backman R., Hupa M. [1999]. Nordic Workshop on Ash Chemistry, Properties and Behavior, June 3-4, Gothenburg, Sweden.

Jimmy Bak [1999], Risø National Laboratory, Denmark (personal communication).

Poul Norby [1999], University of Oslo, Norway (personal communication).

1. A method for improving the combustion, gasification and pyrolysis of biomass, said straw, wood, saw dust, rice husk or peat; alone, mixed, or in any combination with other carbonaceous fuels, said coal, oil, gas, paper or waste. The method comprises the addition of phosphor components to the reactor. The addition may be performed directly or together with the feed fuel, the bed material or the recycle material from the reactor.
2. The phosphor components in claim 1 said in the form of phosphorous acid or orthophosphoric acid or hypophosphorous acid or $H_4P_2O_7$, or said PH_3 , or said oxides of phosphorous or said phosphate compounds of NH_4 , Ca, Mg, Na, K, Fe, Co and Ni, alone or in any mixture hereof.
3. The reactor in claim 1-2 said in the form of a circulating or a bubbling fluid bed reactor.
4. The reactor in claim 1-2 said in the form of a fixed bed reactor or a moving bed reactor.
5. The reactor in claim 1-4 combined with one or more preparation steps said of the type, washing, drying or devolatilization utilized in separate or combined steps before the gasification step.
6. The reactor in claim 1-5 where the maximum temperature is above 500°C.
7. The reactor in claim 1-6 where the pressure is atmospheric or higher.
8. The method of claim 1-7 wherein other additives or bed materials are also used in combination with the additives proposed in claim 2.
9. The method of claim 1-8 wherein a portion of the phosphor containing components produced within the reactor is withdrawn from the reactor and recycled to the reactor to provide said phosphate contained in said a mixture supplied to the reactor.
10. The methods of claim 1-9 wherein a portion of the phosphor-enriched components produced in the reactor is withdrawn from the reactor and utilized as said a mixture used as a fertilizing agent alone or in combination with other fertilizing agents.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/DK 99/00409

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C10L 9/10, C10L 10/04, C05F 11/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C10L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4428310 A (GEORGE T. KEKISH ET AL), 31 January 1984 (31.01.84), column 5, line 4 - line 6, claims 1,4 --	1-9
X	CA 1202485 A (KEKISH, GEORGE T. ET AL), 1 April 1986 (01.04.86), page 2, line 5 - line 14, claims 1-8 --	1-9
A	US 3004836 A (HARRIS THOMPSON), 17 October 1961 (17.10.61), claim 1, example 1 --	1-9
A	SE 418302 B (K. STEENBERG), 18 May 1981 (18.05.81), page 1, line 27 - line 30, claim 1 --	1-9

 Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents	* T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	* X* document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
E earlier document but published on or after the international filing date	* Y* document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	* &* document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means	
P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

Date of mailing of the international search report

12 April 2000

13 04 2000

Name and mailing address of the ISA/

Authorized officer

INTERNATIONAL SEARCH REPORT

International application No.

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4759772 A (EDWARD S. ROGERS ET AL), 26 July 1988 (26.07.88), claims 1,3-4 ---	1-9
A	US 3907674 A (ELLIOTT J. ROBERTS ET AL), 23 Sept 1975 (23.09.75), figure 1, claim 1 ---	3-4

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
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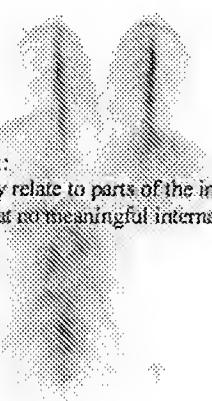
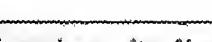
Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US 4428310 A	31/01/84	CA 1184032 A		19/03/85
CA 1202485 A	01/04/86	NONE		
US 3004836 A	17/10/61	NONE		
SE 418302 B	18/05/81	SE 7909208 A		12/02/80
US 4759772 A	26/07/88	CA 1330488 A		05/07/94
US 3907674 A	23/09/75	AU 7835275 A BE 826420 A CA 1012005 A DE 2514046 A DK 174975 A EG 11670 A FR 2268758 A,B GB 1466011 A IT 1030440 B JP 1334493 C JP 50139577 A JP 60055722 B NL 7503189 A NO 139064 B NO 751458 A SE 7502503 A		19/08/76 30/06/75 14/06/77 13/11/75 25/10/75 15/08/77 21/11/75 02/03/77 30/03/79 28/08/86 07/11/75 06/12/85 28/10/75 18/09/78 27/10/75 27/10/75

INTERNATIONAL SEARCH REPORT

International application No.
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Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

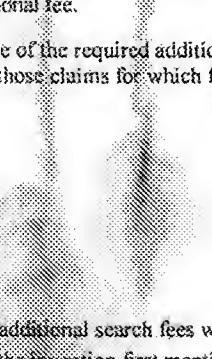
This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:


Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

See extra sheet.

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.: 1-9


Remark on Protest

The additional search fees were accompanied by the applicant's protest.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/DK99/00409

This application contains the following inventions, which are not linked to form a single inventive concept under PCT Rule 13.1 and 13.2:

I. Claims 1-9 relate to methods, components and reactors for improving the combustion, gasification and pyrolysis of biomass involving the addition of phosphor components to the reactor. The process results in phosphor-containing products.

II. Claim 10 relates to a method for using phosphor-enriched components, produced in a reactor for combustion, gasification and pyrolysis of biomass to which phosphor components have been added, as a fertilizing agent.

Observations concerning claims 2-9:

Claims 2-7 belong to a different category than claim 1 to which they refer to (cf. PCT, Preliminary Examination Guidelines, III, 3.1 and 3.2). Further, claims 8-9 belong to different categories than claims 2-7. The search has not covered the aspect that one or more of claims 2-9 might be independent claims. If this was the case, then the application would contain additional inventions to the two inventions mentioned above. None of claims 2-9 have been searched independently. Claims 2-9 have been recognized as dependent claims referring to the method of claim 1 and have been searched as such. That is, claims 2-9 have for search purposes been regarded as if they included all the features of claim 1.